

Supplemental Information for:
**Carbonate Radical Formation in Radiolysis of Sodium
Carbonate and Bicarbonate Solutions up to 250° C and the
Mechanism of its Second Order Decay**

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A. Calculation of Bicarbonate Equilibria at High Temperature

The analysis of the carbonate/bicarbonate/carbonic acid system is based on the temperature-dependent acid-base equilibrium constants given in table 1. At elevated temperatures, the system equilibrium strongly shifts away from carbonate ion toward bicarbonate and carbonic acid and ultimately CO₂. For instance, in “natural pH” solutions of sodium bicarbonate of various concentrations at 250°C only a fraction, roughly 50%, of the initial bicarbonate remains.

In order to properly estimate the actual bicarbonate concentration the system in Table 1 is solved:

$$[H_2CO_3] = \frac{K_w [HCO_3^-]}{K_1 [OH^-]} \quad (1)$$

$$[CO_3^{2-}] = \frac{K_2 [OH^-] [HCO_3^-]}{K_w} \quad (2)$$

$$[CO_2] = \frac{K_d [HCO_3^-]}{[OH^-]} \quad (3)$$

Using the charge balance (4) and the conservation of (carbon) mass (5), we can also determine the HCO₃⁻ concentration (6):

$$[H^+] + [NaHCO_3]_o = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (4)$$

$$[NaHCO_3]_o = [CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (5)$$

$$[HCO_3^-] = \frac{[NaHCO_3^-]_o + \frac{K_w}{[OH^-]} [OH^-]}{1 + \frac{2K_2 [OH^-]}{K_w}} \quad (6)$$

To determine the OH⁻ concentration, the roots of the quartic equation (5) are solved :

$$c_1 [OH^-] + c_2 [OH^-]^2 + c_3 [OH^-]^3 + c_4 [OH^-]^4 + c_0 = 0 \quad (7)$$

$$c_0 = \frac{K_w^2}{K_1} - K_w K_d \quad (7a)$$

$$c_1 = \frac{K_w [NaHCO_3]_o}{K_1} + K_d [NaHCO_3] + K_w \quad (7b)$$

$$c_2 = K_2 - K_d - \frac{K_w}{K_1} \quad (7c)$$

$$c_3 = -\frac{K_2 [NaHCO_3]}{K_w} - 1 \quad (7d)$$

$$c_4 = -\frac{K_2}{K_w} \quad (7e)$$

Table 1: Parameters Used in the Calculation of HCO_3^- and CO_3^{2-} Concentrations

Reaction ^a Formula ^b	Reference
$\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$ $pK_w = 14.93 - 0.04131t + 1.9 \times 10^{-4}t^2 - 4.705 \times 10^{-7}t^3 + 5.724 \times 10^{-10}t^4$	Elliot et al. (1994) ¹
$\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-$ $pK_1 = 1234.4 + 68608/T + 193.4 \ln T - 0.1642T - 3747 \times 10^6 / T^2$	Park et al. (1998) ²
$\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-}$ $pK_2 = -14.44 + 5.188 \times 10^{-2}T - 3.27 \times 10^{-5}T^2 + 3644.8 / T$	Patterson et al. (1984) ³
$\text{HCO}_3^- \rightarrow \text{CO}_2 + \text{OH}^-$ $pK_d = 3.0 \times 10^{-8}t^3 - 4.0 \times 10^5t^2 + 0.0287t - 8.3597$	SUPCRT92 Johnson et al (1992) ⁴

^aUnits: $\text{M}^{-1}\text{s}^{-1}$ for rate constants and mol kg^{-1} or kg mol^{-1} for equilibrium constants. ^b T is the temperature in Kelvin, t in Celcius.

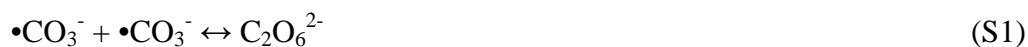
Table 2: Percentage of bicarbonate remaining in solution

T (°C)	% of Bicarbonate Remaining			
	0.001 M	0.002 M	0.02 M	0.1 M
0	98.6	98.6	98.6	98.6
25	97.1	97.1	97.1	97.1
50	96.5	96.6	96.6	96.6
75	95.3	95.7	95.9	95.9
100	93.3	94.2	94.8	94.8
125	90.1	91.8	93.2	93.3
150	85.5	88.1	90.8	90.8
175	79.1	82.9	86.9	87.0
200	70.5	75.4	80.7	80.9
225	59.3	65.0	70.7	70.9
250	45.5	50.9	55.7	55.8

- (1) Elliot, A. J. "Rate Constants and G-Values for the Simulation of the Radiolysis of Light Water over the Range 0-300°C," *AECL*, **1994**.
- (2) Park, S. N.; Kim, C. S.; Kim, M. H.; Lee, I. J.; Kim, K. *Journal of the Chemical Society-Faraday Transactions* **1998**, *94*, 1421.
- (3) Patterson, C. S.; Busey, R. H.; Mesmer, R. E. *Journal of Solution Chemistry* **1984**, *13*, 647.
- (4) Johnson, J. W.; Oelkers, E. H.; Helgeson, H. C. *Computers & Geosciences* **1992**, *18*, 899.

B.) Summary of Gaussian calculations

To study the formation of peroxydicarbonate from the recombination of two carbonate radicals (reaction S1 below), electronic structure calculations were performed using *Gaussian03*.¹ We were interested in the thermochemistry of the postulated peroxydicarbonate intermediate. We compared results for gas-phase calculations and the polarized continuum model based on the integral equation formalism, selected using the keywords `scrf=(iefpcm,solvent=water)`. When explicitly including hydrogen—e.g., in water molecules—it was necessary to use the UFF force field to define radii for the hydrogens in the continuum cavity. The keywords `scrf=(iefpcm,solvent=water,read)` were included in the route section of the input file, and the keywords `radii=uff` were placed after the molecule specification section.



Finding the lowest energy geometry of $\text{C}_2\text{O}_6^{2-}$ is nontrivial. Relaxed potential energy scans of the COOC dihedral angle were carried out using both density functional theory (B3LYP) and second order Moeller-Plesset perturbation theory (MP2). In each case, we used Dunning's correlation-consistent double zeta basis set augmented with diffuse functions (aug-cc-pvDZ). The COOC dihedral angle was incremented in steps of -10° from 180° to 0° . The energy varied by less than 1 kJ/mol for dihedral angles of $180^\circ \pm 60^\circ$. This flat potential energy surface gave rise to a number of low frequency vibrations in the subsequent normal mode analyses. In all cases, the low frequency vibrations were included in calculating the zero-point energies. We preferred to use a higher level of theory such as QCISD; however, the relatively flat energy surface gave rise to convergence problems, because the QCISD method numerically calculates second derivatives. In some cases, we used the composite Gaussian-3 (G3) method to compare the other methods.

Table S1 summarizes the enthalpies and free energies of reaction S1 calculated at the indicated levels of theory. One should note that reaction S1 is significantly endothermic in the gas phase, largely due to the coulombic repulsion of the two anions. In the polarized continuum model, the reaction is more favorable by almost 300 kJ/mol. The MP2 and G3 calculations predict the free energy to be almost thermoneutral.

The continuum solvent plays a decisive role in stabilizing the peroxydicarbonate dianion. In the real system, there is great potential for peroxydicarbonate to form hydrogen bonds with the solvent, or for acid-base equilibria to change the reaction pathway. We briefly investigated the latter issue. We protonated one carbonate radical and calculated the thermochemistry for the following reaction



We investigated three possible geometries for HC_2O_6^- (illustrated in Figure S1), although there are potentially other stable configurations. The thermochemical results are presented in Table S2. Reaction S2 is more favorable than reaction S1—particularly in the gas-phase, where the proton removes charge repulsion of the reactants.

However, we do not believe a proton is actually involved in the aqueous reaction, given the acidity of the carbonate radical^{2,3}. The more likely scenario involves stabilization of the radicals and/or peroxydicarbonate by hydrogen bonding. Inclusion of specific water molecules in the calculation is beyond the scope of the present investigation.

Table S1. Thermochemical data for the reaction forming peroxydicarbonate from two carbonate radicals. Except for the G3 calculation, the basis set was aug-cc-pvDZ.

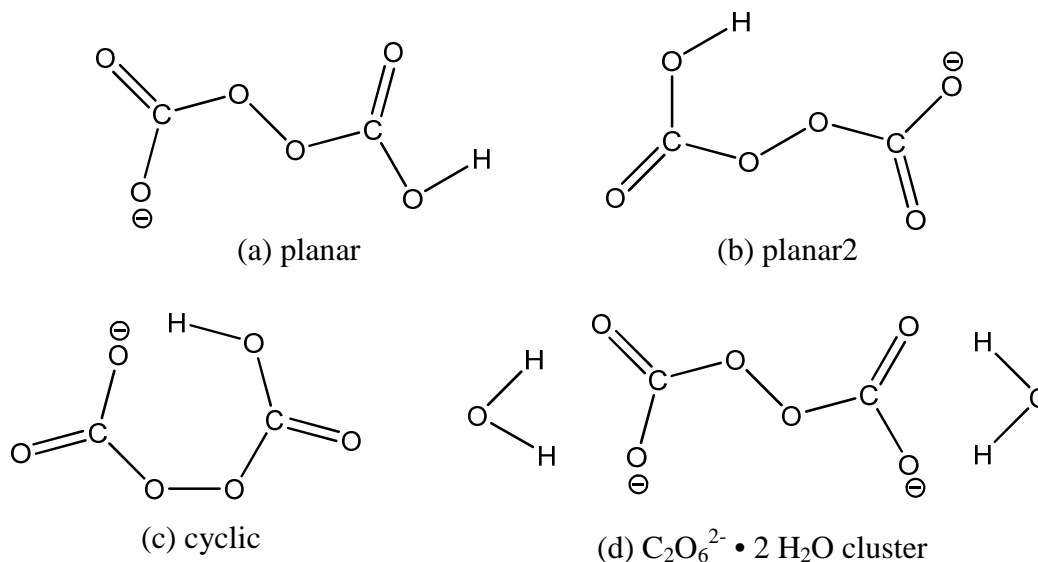
Model	$\Delta_{rxn}H^\circ$ (kJ/mol)		$\Delta_{rxn}G^\circ$ (kJ/mol)	
	gas	PCM	gas	PCM
B3LYP	314.25	8.92	358.96	54.81
MP2	236.16	-58.08	275.38	-12.27
QCISD	247.93		297.06	
G3	219.20	-71**	269.26	-21**

** For the G3 calculations, PCM entries in the table were calculated by subtracting 290 kJ/mol from the gas-phase results, which is the approximate solvation energy in the B3LYP and MP2 calculations.

Table S2. Thermochemical data for the reaction between the carbonate and bicarbonate radicals. In all cases, the basis set was aug-cc-pvDZ.

Model	$\Delta_{rxn}H^\circ$ (kJ/mol)		$\Delta_{rxn}G^\circ$ (kJ/mol)	
	gas	PCM	gas	PCM
B3LYP (planar)	-69.24	-38.59	-14.67	9.51
B3LYP (planar2)	-107.44		-53.07	
B3LYP (cyclic)	-126.07	-30.13	-71.41	24.67
MP2 (planar)	-153.56	-118.50	-100.95	-68.03
MP2 (planar2)	-193.94	-108.82	-141.88	-59.06
MP2 (cyclic)	-212.33	-107.78	-159.91	-53.46

Figure S1. Three possible geometries for HC_2O_6^- (a-c), and a cluster with peroxydicarbonate and two water molecules (d).



(1) Gaussian 03, Revision C.02. Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford, CT, 2004.

(2) Czapski, G.; Lyman, S. V.; Schwarz, H. A. *Journal of Physical Chemistry A* **1999**, *103*, 3447.

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